

PATENT SPECIFICATION

NO DRAWINGS

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919,500



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COMPLETE SPECIFICATION

Improvements relating to Bonded Fibrous Sheet Material and its production

We, E. I. DU PONT DE NEMOURS AND COMPANY, a Corporation organised and existing under the laws of the State of Delaware, United States of America, located at
5 Wilmington 98, State of Delaware, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 This invention relates to novel fibrous sheet materials which have a unique combination of properties including flexibility, high mechanical strength and moisture permeability and to their production, and is an improvement in or modification of the invention described in Specification No. 23030/59. (Serial No. 914,712).

15 Specification No. 23030/59 (Serial No. 914,712) describes sheet material comprising a ligated fibrous mate comprising at least 50%, based on the weight of fibres in the mat, of *in situ*-retracted artificial fibres, the mat having been shrunk by 30%—80% of its original planar area, and dispersed throughout the mat
25 10%—90%, on the same basis, of a synthetic polymer binder for the fibres in a form such that in the absence of the fibres it would have a tensile stress at 5% elongation of 5—150, preferably 5—50 pounds per square inch
30 (p.s.i.). These materials have in general the properties of soft leather suedes and may be used with advantage to replace these products of natural origin.

35 It has now been found that useful products of the type described in Specification No. 23030/59 (Serial No. 914,712) can also be obtained when one or more of the limiting factors set out above is extended in certain directions and by certain degrees. More particularly the degree by which the mat is shrunk
40 is 30—90%, and the mat contains 10—70% of the binder based on the combined weight of the fibres and the binder.

The use of the term "binder" is not in-

tended to imply that the impregnating polymer necessarily adheres to their fibres. Indeed, in the embodiments of the invention specifically described there is substantially no such adhesion, and some at least of the valuable properties of the products are doubtless attributable to this fact.

The finished product has a degree of suppleness not achieved by prior art high strength non-woven mats bound with a synthetic polymer. This degree of suppleness is defined as being less than 65 p.s.i. (This and all figures for suppleness given in this Specification are as determined by the cantilever test described in ASTM D 1388—55T). The suppleness is expressed as bending stiffness in pounds per square inch, obtained by dividing the cantilever value by the cube of the thickness of the material.

Tensile stress is defined as the force per unit of original cross-sectional area required to stretch the specimen to a stated elongation. It is expressed as pounds per square inch of the original cross-sectional area (p.s.i.) at the stated elongation.

The shrinking of the mat is done with hot water or other means capable of retracting the fibres without fusing or damaging them. The binder is preferably introduced into the mat in the form of a solution or aqueous dispersion. It is to be understood, however, that the binder can be introduced into the mat by other techniques, e.g., distributing it throughout the mat in the form of dry powder or as a slurry of fibrils. After the binder is introduced into the shrunken mat in the form of solution or dispersion, it is coagulated by immersing the mat in a coagulant or other appropriate means after which the mat is dried. In the case of the solution-impregnated mats, the solvents for the binder are washed out of the mat before drying. A nap is raised on one or both faces of the product when a suede material is desired.

As the invention is described in greater detail, it will be seen that some embodiments of the process will include such steps as roller squeezing or wringing the wet mat after it is impregnated and again after it is bathed; hot pressing the mat before or after it is impregnated; dyeing the mat, buffing and brushing it at any convenient point in the process; or treating the product with various known fabric finishing materials such as softeners, water repellents, and flexible polymeric surface coatings.

By the term "ligating" is meant the binding together of adjacently disposed fibres lying substantially parallel to the plane of the mat (or the faces of the mat) by forcibly orienting sufficient fibres to a position substantially perpendicular to the plane of the mat so that a unitary, dense coherent structure is formed. In the present invention, the fibre orientation is preferably accomplished by punching the mat with fine barbed needles, which are mounted in a conventional needle loom.

The fibrous mat can be composed of both non-retractable fibres and retractable fibres. In the case of mats made from such blends of fibres, sufficient retractable fibres must be used to bring about the desired planar shrinkage. The amount of shrinkable fibres required will vary from fibre to fibre depending upon the shrinkability of the fibre and the force exerted during its retraction. The retraction may result from a simple reduction in length, or from distorting or crimping of the fibres into an irregular shape.

Especially desirable results in making suede materials are obtained with polyethylene terephthalate fibres prepared in accordance with the teaching of Specification No. 712,950 or United States Specification No. 2,758,908. These polyester fibres have the property of

retracting when heated in hot water or in hot air below their bonding temperature. When crimped, the fibres have a wool-like appearance and resilience, and are desirably interlocked in the mat. Another type of retractable filamentary material that can be used is a regenerated cellulose fibre of the kind described in United States Specification No. 2,515,834. These fibres crimp spontaneously at room temperature in a swelling agent, such for example as an aqueous alkali. Liquid ammonia will cause retraction, by shrinkage rather than crimp formation, of ordinary viscose rayon, which also can be used in preparing the products of this invention.

Methods are known whereby other artificial polymeric fibres can be manufactured so as to have the necessary retraction characteristics, including polytetrafluoroethylene, cellulose acetate, nylon, 40/60 copolymer of acrylonitrile and vinyl chloride, 10/90 copolymer of vinyl chloride and vinylidene chloride, polyethylene and polystyrene. These methods involve spinning the fibres and then stretching them, the degree of stretch, taken in association with any other treatments to which the fibres may be subjected, e.g., partial relaxation, determining the degree of retractability. More detailed information can be obtained, for example, from Specifications Nos. 712,950 and 875,052, and United States Specifications Nos. 2,336,797, 2,515,834 and 2,910,763. These other fibrous materials can be used alone or blended with each other. The preferred polyethylene terephthalate fibre can be blended with any of the aforementioned fibres.

The following Table illustrates retraction media, times, temperatures and amounts of retraction for needled unimpregnated mats for various fibres listed above for a given denier:

TABLE I

| Fibre and Denier | Retraction Medium — Temperature | Specific Gravity | | Time (Minutes) of Exposure in Retraction Medium | % Planar Area Loss of Mat |
|--|---------------------------------|-------------------|------------------|---|---------------------------|
| | | Before Retraction | After Retraction | | |
| Cellulose acetate, 2 denier staple | 49% Aqueous acetone—20°C. | 0.09 | 0.14 | 0.5 | 69 |
| Nylon, 6 denier staple | Dilute nitric acid — 20°C. | 0.09 | 0.10 | 1.0 | 55 |
| 40/60 Acrylonitrile/vinyl chloride copolymer, 5 denier staple | Air — 150°C. | 0.11 | 0.12 | 5.0 | 41 |
| 10/90 Vinyl chloride/vinylidene chloride copolymer, 25 denier staple | Air — 170°C. | 0.19 | 0.28 | 5.0 | 77 |
| Polyethylene, 6 denier staple | Water — 100°C. | 0.17 | 0.26 | 0.5 | 80 |
| Polystyrene, 4 denier | Air — 110°C. | 0.10 | 0.18 | 5.0 | 60 |
| Polytetrafluoroethylene 3—5 denier staple | Air — 300°C. | — | — | 60.0 | 40 |
| Polytetrafluoroethylene 3—5 denier staple | Air — 325°C. | — | — | 270.0 | 75 |

5 In the case of those fibres which tend to be dissolved in the solvent for the binder, it is desirable to reduce the solvent action of the solvent by incorporating a non-solvent, e.g., water, a glycol or an alcohol up to the point of incipient gelation of the binder and then after impregnating the mat, immediately coagulating the binder throughout the mat in order to remove the solvent from further contact with the fibres.

10 Non-retractable fibres employed in admixture with the retractable fibres may be natural or artificial, straight or crimped fibres.

15 The amount of non-retractable blending fibres to use in any particular case will be governed largely by the intended use of the product, and the retraction capacity and efficiency of the shrinkable fibre.

20 The denier of the retractable fibres is preferably no higher than 1.5, and those having a denier of about 0.5 to 1.0 are particularly preferred. Somewhat coarser fibres are sometimes desirable in the suede type products to

25 modify the nap characteristics. Although long fibre and even continuous filaments can be used to make the products of this invention, fibres varying in length from about 0.5 inch to about 3 or 4 inches are usually employed, and 1.0 to 1.8 inch fibres are preferred. Shorter fibres tend to reduce the products' tensile and tear strengths and longer fibres are more difficult to handle in mat formation.

30 The fibres are formed into a loose mat of convenient thickness in any known manner. In most cases the initially formed mat will weight from about 4 to 10 ounces per square yard. Although the carding method is preferred, the mat may for example also be formed on a foraminous carrier from a liquid suspension of fibres, or blown or dropped from an air suspension. Cross-lapping the fibres into layers of dissimilar orientation within the plane of the mat provides equalised contraction of the mat in the subsequent shrinking step, and a product having balanced stretchability. When unidirectional stretchability is preferred, the

cross-lapping is of course not employed, that is, most of the fibres are so laid that they have similar orientation in the plane of the mat.

During the important needling step the loose mat is converted into a uniformly dense and smooth felt-like structure by the barbed needles. The needles force numerous fibres, singly or in groups, into positions more or less perpendicular to the faces or plane of the mat, rendering the mat compact and coherent. Each square inch of the mat should preferably receive about 1500—3800 needle punches, referred to as perforation density. This is best accomplished stepwise on alternate sides of the mat in about 8 to 20 passes through a conventional needle-loom. Too low a perforation density yields a loose mat of coarse texture, while excessive needling tends to roughen, stiffen and weaken the mat. The needled mats before shrinking usually have a specific gravity in the range of 0.08 to 0.19, and preferably about 0.13 to 0.15.

The densification of the needled mat consequent on the shrinking treatment supplements the compaction caused by needling to produce a tightly tangled mass of fibres in which the needle marks are substantially obscured. The specific gravity of the shrunk mat is usually about 0.10 to 0.28 gram./cc. Excessive shrinkage gives a high density web which results in a slow rate of impregnation and detracts from the product's suppleness. Insufficient shrinkage on the other hand makes for a low density product that is sleazy, weak and dimensionally unstable. The mat is considerably more soft and supple after being properly shrunk.

If the needled mat is heated suddenly it tends to pucker or wrinkle, probably as the result of the outer layer of fibres shrinking before the inner layer. To ensure a smooth wrinkle-free product, therefore, the mat is shrunk gradually. This is conveniently accomplished in the case of retractable polyethylene terephthalate fibres by dipping the mat in water heated to about 170°—175°F.

The shrunk mat of tightly interlocked retracted fibres is coherent, strong and dense, yet soft, smooth and flexible. It has a fine uniform porous texture. Drying the mat before impregnating it with the binder tends to enhance its smoothness. It is important that the mat be shrunk before impregnation, since the solvents for the impregnating binder inhibit retraction of the fibres.

If a binder which has tensile stress at 5% elongation outside the 5—150 p.s.i. range is used as the impregnant for the non-woven mats, there are obtained products having a bending stiffness greater than 65 p.s.i.

The particularly preferred range for the tensile stress at 5% elongation of the binder as present in the mat is 10—50 p.s.i. The particularly preferred binder is an elastomer formed by employing a compound having 2 active hydrogen atoms bonded to amino-

nitrogen atoms to chain-extend the reaction product of a polyalkylene ether glycol and an organic diisocyanate. Such an elastomer has the advantages of having high tensile strength without requiring a curing agent, and of not requiring a plasticiser to achieve the necessary softness, flexibility and elasticity. Furthermore, it is not deleteriously affected by most solvents, soaps, detergents and other materials used in laundering clothes. When solutions of the elastomer are deposited uniformly throughout a fibrous mat in accordance with the method of this invention, the product has a spongy microporous structure.

The especially preferred elastomers useful as impregnants in carrying out this invention can be prepared by first preparing a prepolymer having terminal —NCO groups by mixing a polyalkylene ether glycol with an organic diisocyanate and heating at about 50 to 120°C. whereby a prepolymer is formed having terminal —NCO groups, and then chain-extending the prepolymer. Alternatively, the diisocyanate can be reacted with a molar excess of the glycol, and the product capped by reacting it with more diisocyanate, after which the resulting product is chain-extended. The preparation of such elastomers is described in greater detail in our Specification No. 38723/56 (Serial No. 849,154). Polyalkylene ether glycols having a molecular weight of 900 to 3000 are preferred. Polyurethanes formed from polytetramethyleneether glycol or polypropyleneether glycol and tolylene-2,4-diisocyanate and chain-extended with hydrazine are particularly preferred.

The binder is preferably dissolved in sufficient solvent to give a solution of relatively low viscosity, preferably less than about 3 poises for rapid impregnation. Any good solvent for the binder, preferably one which is completely water-miscible or nearly so, can be used, so long as it does not seriously attack any of the fibres of the mat. While N,N-dimethyl-formamide is preferred with the polyurethane binders described above, other useful solvents include, for example, dimethyl sulphoxide, tetrahydrofuran, tetramethyl urea, N,N-dimethyl-acetamide and mixtures of these compounds. Acetone is useful as a diluent following polymerisation.

The mat is dipped into the binder solution, or the solution is applied to the mat until the mat is substantially saturated with the solution. The mat is then drained or squeezed free of excess solution, so that no free solution remains on the surface and the mat contains 10 to 70% by weight of binder solids based on the combined weight of binder and fibre in the mat. Excessive binder makes the product rubbery. Too little, on the other hand, results in a sleazy product with poor strength, elasticity and dimensional stability. Mat density, concentration and viscosity of the impregnating solution, and the extent of squeezing or

draining after impregnation, are all factors which control the binder content of the mat.

When the binder is introduced into the mat as a solution, it is preferably coagulated or precipitated by extracting the solvent with a liquid which is miscible therewith but is a non-solvent for the binder and the material of the fibres. Water will generally be used for this purpose, though a glycol or alcohol, for example, could be used if desired. The water or other non-solvent liquid may be applied to the mat for example by immersion or spraying. In most cases the coagulation is substantially complete within about 30 seconds of treatment, but continued treatment with the non-solvent is necessary to flush all or most of the solvent from the mat. If more than about 5% of solvent, based on the elastomer content within the mat, remains after the water treatment, the product cannot be subjected to elevated drying temperatures without destroying its suppleness.

After the impregnated mat has been washed sufficiently to remove all or nearly all of the solvent, it is force dried with the aid of heat, preferably by means which further improve its smoothness. The drying can be performed in an oven, by passing the mat over smooth heated rotating drums, or by known web-drying methods. For some purposes, the product is now complete except for buffing. When a coloured product is desired, a dyeing step is included at any convenient stage in the process.

When a denser product is wanted, the dried sheet is pressed between two smooth heated surfaces. The time, temperature and pressure of pressing are controlled to maintain product permeability and suppleness, as will be apparent to those skilled in the art.

A nap can be raised on one or both sides of the smooth, supple microporous sheet in any suitable manner known in the art of napping fabrics and tanned skins. A preferred napping process involves buffing with emery covered rolls followed by brushing. Buffing actually improves the suppleness of the product besides softening its surface feel. It was surprising and unexpected that a soft downy nap of uniform appearance could be raised on a non-woven mat impregnated with an elastomer of low tensile stress.

Another optional step is to treat the product, or the mat at any stage of the process, with known fabric softeners.

It is to be understood that the above-specified steps of needling, shrinking and elastomer impregnating of the retractable mat are the indispensable steps in the process of this invention. Such steps as buffing, brushing, dyeing and pressing, while advantageous in many cases, are optional, and may be included in the process at any convenient point, either prior to or after the impregnating operation.

Printing, stencilling, embossing, preferential

dyeing, and other known techniques for surface decoration can be used to modify the product.

The products of this invention, because of their many desirable properties, are eminently suited also for use as a substrate to be coated with any of a multitude of known coating compositions. For example, useful supply sheet materials will result from applying a flexible layer of permeable or impermeable coatings to one or both sides of the napped or plain product. Surface coatings based on vinyl chloride polymers or copolymers are particularly useful. Moisture permeable coatings based on vinyl chloride polymers or polyurethane elastomers are of particular interest, such for example as those disclosed in Specification No. 788,560 or 3235/59 (Serial No. 914,711), or various synthetic rubbers, e.g. neoprene, butadiene/styrene copolymers or butadiene/acrylonitrile copolymers. Soft and moisture permeable leather-like materials can be produced in this manner.

From the foregoing detailed description, it will be apparent that the process and product of this invention have important advantages which represent an advance in the art of making sheet materials. The process is practical, economical and readily adaptable to mass production. The invention provides a durable permeable sheet material of extraordinary softness and suppleness. There is also provided a napped garment material of remarkably pleasant hand. The elastic macroporous suede-like sheet has unsurpassed appearance and comfort features. Obtainable in an unlimited array of colours, and relatively uniform in properties from batch to batch, the product can be made in almost any width and in any length. Long lengths are conveniently shipped and stored in roll form. Garments made from the product not only withstand repeated laundering, but are even softer to touch after such exposure. They also withstand ordinary dry cleaning. The material has good resistance to soiling and to wrinkling.

The principal use for the products of this invention, as previously indicated, is in the apparel industry as a material for making all sorts of garments. Other uses for the products are as filter media, insulation, table and roll coverings, sound and vibration absorbents, liners and paddings for blankets, carpets, sleeping bags, garments and the like, and as special-purpose upholstery materials. Another important use is for the uppers of both men's and women's suede shoes. In addition, they are useful as replacements for polishing felts and chamois.

The following Examples illustrate the invention; unless otherwise stated, parts and proportions are by weight.

EXAMPLE I

9 Parts of 1.5-inch polyethylene terephthalate fibres capable of retracting about

- 70% of their drawn length and treated with a cationic softener are blended with 1 part of 1.5-denier, 1.5-inch crimped staple fibres of polyethylene terephthalate and carded and cross-lapped into a loose non-woven mat. (The addition of a proportion of crimped fibres aids in the carding, blending and holding together of the other fibres prior to the shrinking step, and is generally advisable when such other fibres are of a denier substantially below 1.0). The mat is needle punched to yield a ligated mat having a density of about 0.10 g./cc. The mat is then immersed in water at about 174°F. for about 3 minutes to shrink it to about 53% of its original planar area. Next, the shrunken mat is drained free of water and heated at about 250°F. until it is substantially dry. The shrunken and dried mat has a density of about 0.13 g./cc.
- The dried mat is next impregnated with a 15% N,N-dimethylformamide solution of a polyurethane elastomer obtained as follows:—
- 73.5 Parts of polytetramethylene ether glycol of molecular weight 1000 are dimerized with 6.4 parts of tolylene-2,4-diisocyanate by mixing together and heating for 3 hours at 194°F. The resulting low polymer is capped with methylene-bis(4-phenyl isocyanate) by mixing 6.4 parts of the former with 18.4 parts of the latter and heating for 1 hour at 176°F. The capped low polymer, a prepolymer with isocyanate end groups, is dissolved in sufficient N,N-dimethylformamide to form a 20% solu-

tion. Separately, a 20% solution of hydrazine hydrate is prepared with the same solvent. Dibutylamine is added to the hydrazine hydrate solution in amount 0.15% of the hydrazine hydrate present; this serves as a chain-stopper. The two solutions are then mixed together to form a 20% elastomer solution. For the impregnating operation to follow, the solution is diluted with N,N-dimethylformamide to an elastomer content of about 15%.

After excess impregnant has been removed from the surface of the mat by the squeeze roll, the impregnated mat is immersed in water at about 75°F. until the binder is coagulated throughout the mat. The resulting sheet material is then passed through wringer rolls which exert sufficient pressure on the mat to remove as much water and solvent as possible without crushing or otherwise damaging the mat. After passing between the wringer rolls, the resulting product is washed with water until it is substantially free of solvents for the binder. Next, the impregnated mat is dried and smoothed on drums heated to about 275°F. to yield a sheet material having a density of about 0.3 to 0.35 g./cc. and a ratio of binder to the total weight of fibres and binder of 60%.

The resulting sheet material is finally buffed to raise a downy nap on its surface, brushed lightly and dyed to yield a moisture-permeable, suede-like product having the following properties:

| Per Cent Binder Based on Combined Weight of Fibre and Binder | |
|---|------------------|
| | 60% |
| Weight | 9—10 oz./sq. yd. |
| Thickness | 40 mils |
| Density | 0.30—0.35 g./cc. |
| Bending Stiffness | 6—8 p.s.i. |

- A 10-mil thick film is prepared by coating the impregnating solution described above on a glass plate and then, before any appreciable amount of solvent has evaporated, the glass plate with the film thereon is immersed in water at 24°C. for about 30 minutes to coagulate the polymer and extract the solvent. The

film, stripped from the plate, is then dried in an oven at about 120°C. The film, which is in substantially the same form as the binder in the product of this Example, has a tensile stress at 5% elongation of 21 pounds per square inch.

EXAMPLE II

- A non-woven needle punched mat of 0.8 denier polyethylene terephthalate fibres having a density of about 0.10 g./cc. is immersed in hot water to shrink the mat about 85% in area. Next, the product is dried to yield a shrunken mat having a density of about 0.18 g./cc. The shrunken mat is next impregnated

with a 7.5% N,N-dimethylformamide solution of the polyurethane elastomer as described in Example I, then the impregnant therein is coagulated as described in that Example. Finally, the impregnated mat is buffed and dyed to yield a moisture-permeable, suede-like sheet material having the following properties:

| | |
|---|---------------|
| Per Cent Binder Based on Combined Weight of Fibre and Binder | 26% |
| Weight | 7 oz./sq. yd. |
| Thickness | 40 mils |
| Density | 0.24 g./cc. |
| Bending Stiffness | 6—8 p.s.i. |

- As has already been said, our Specification No. 23030/59 claims a flexible moisture-permeable sheet material which comprises a ligated fibrous mat comprising at least 50%, based on weight of the fibres in the mat, of *in situ*-retracted artificial fibres, said mat having been shrunk by 30% to 80% of its original planar area, and dispersed throughout said mat 10—90% on the same basis of a synthetic polymer binder for said fibres in such a form that in the absence of the fibres it would have a tensile stress at 5% elongation of 5 to 150 pounds per square inch.
- This subject matter is not claimed here. Subject to the foregoing disclaimer,
WHAT WE CLAIM IS:—
1. A flexible moisture-permeable sheet material which comprises a ligated fibrous mat comprising at least 50%, based on the weight of the fibres in the mat, of *in situ*-retracted artificial fibres, said mat having been shrunk by 30% to 90% of its original planar area, and dispersed throughout said mat 10—70% of a synthetic polymer binder for said fibres, (based on the combined weight of the fibres and the binder), said binder being in such a form that in the absence of the fibres it would have a tensile stress at 5% elongation of 5 to 150 pounds per square inch.
 2. Material according to claim 1, wherein the binder is formed by chain-extending the reaction product of a polyalkyleneether glycol and an organic diisocyanate with a compound having two active hydrogen atoms bonded to amino-nitrogen atoms.
 3. Material according to claim 2, wherein the polyalkyleneether glycol is polytetramethyleneether glycol or polypropyleneether glycol.
 4. Material according to claim 2 or 3, wherein the diisocyanate is tolylene-2,4-diisocyanate.
 5. Material according to any of claims 2—4, wherein the polyalkyleneether glycol has a molecular weight of 900 to 3000.
 6. Material according to any of claims 2—5, wherein the chain-extending agent is hydrazine.
 7. Material according to any of the preceding claims, wherein the artificial fibres are polyethylene terephthalate fibres.
 8. Material according to any of the preceding claims, wherein the artificial fibres have a denier of less than 1.5 and a length of about 0.5 to 4 inches.
 9. Material according to claim 8, wherein the fibres have a denier of about 0.5 to 1.0 and a length of about 1 to 1.8 inches.
 10. Material according to any of the preceding claims, wherein the mat is made up of two or more layers in which the fibres are dissimilarly orientated in the plane of the mat.
 11. Material according to any of the preceding claims, comprising also a flexible permeable polymeric surface coating.
 12. Material according to claim 11, wherein the polymer in the surface coating is a vinyl chloride polymer or a polyurethane elastomer.
 13. A flexible moisture-permeable sheet material according to claim 1, substantially as hereinbefore described.
 14. A method of making a flexible moisture-permeable sheet material claimed in any of the preceding claims, which comprises ligating a fibrous mat comprising at least 50% of the artificial retractable fibres (based on the weight of fibres in the mat), treating the mat with means effective to retract said fibres and thereby cause the mat to shrink by 30% to 90% in planar area, and distributing throughout said mat a dispersion of the synthetic polymer binder in sufficient quantity to deposit 10 to 70% solid polymer based on the combined weight of fibres and binder in the mat.
 15. Process according to claim 14, wherein a loose mat is formed from staple fibres and is ligated by punching with needles having barbed blades to force numerous closely spaced fibres into positions substantially perpendicular to the faces of the mat whereby the mat becomes dense and coherent.
 16. Process according to claim 14 or 15, wherein the ligated mat has a specific gravity of 0.13—0.15 before the shrinking operation.
 17. Process according to any of claims 14—16, wherein the ligated mat has a perforation density of 1500—3800 before the shrinking operation.
 18. Process according to any of claims 14—17, wherein the mat is shrunk by treating it with hot water.
 19. Process according to any of claims 14—18, wherein the shrunk mat is impregnated with a solution of the binder in an organic solvent after which the binder is precipitated

and the solvent substantially completely extracted from the mat by means of a liquid which is miscible therewith but is a non-solvent for the binder and the material of the fibres.

- 5 20. Process according to claim 19, wherein the organic solvent for the binder is water-miscible, and the binder is precipitated and the solvent extracted with water.

- 10 21. Process according to claim 19 or 20, wherein the organic solvent is N,N-dimethylformamide.

22. Process according to any of claims 19—

21, wherein the mat is subsequently freed from the precipitating and extracting liquid by heating.

23. A method of making a flexible moisture-permeable sheet material according to claim 14 substantially as described in either of the foregoing Examples.

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